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13. ABSTRACT ***(Maximum 200 Words)***

Electrochromic and conducting polymers may prove especially important for a number of Air Force applications including chameleon coatings, informational displays, IR and microwave attenuation, dialed tint windows, and gap sealants. We are developing conjugated, redox active, and conducting polymers with controllable electronic band gaps that range from 1.1 eV to 4.0 eV, thus spanning from the NIR, through the entire visible spectrum, and into the UV. We have developed a reproducible method by which electrochromic coloration efficiencies (CE) can be measured accurately for polymer films. We have investigated the use of BF_3 ethyl etherate as an alterative media for the electrochemical synthesis of highly electroactive polymer films and shown it to be applicable to preparing high quality polythiophene and donor-acceptor polymers which can be n-type doped.. Electrochromic devices (ECD's) with especially high color contrasts between bleached and colored states have been developed. We have broadened the visible absorption in polymer ECD's while retaining the high contrast by having two cathodically coloring polymers with different λ_{max} values deposited as a bilayer on a single electrode. Functionalized 3,4-propylenedioxythiophene polymers have been developed as soluble conducting polymers for blending into elastomeric hosts and as solution processable high contrast electrochromic polymers. We have prepared multi-color electrochromic and red emitting polymers through the synthesis of soluble low band gap polymers containing conjugated donor and acceptor units.

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Controlled Redox and Electrical Properties in Polyheterocycles

Reporting Period:

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1. Objectives

The effect of macromolecular structure and redox switching between charge states has been used to control the optoelectronic properties of conjugated polymers. Specific properties investigated include structure:property effects via model compounds, electrochromism, switchable electrical conductivity, and switchable IR and microwave absorption.

2. Status of Effort

Electrochromic and conducting polymers may prove especially important for a number of Air Force applications including chameleon coatings, informational displays, IR and microwave attenuation, dialed tint windows, and gap sealants. We are developing conjugated, redox active, polymers with controllable electronic band gaps that range from 1.1 eV to 4.0 eV, thus spanning from the NIR, through the entire visible spectrum, and into the UV. We have developed a reproducible method by which electrochromic coloration efficiencies (CE) can be measured accurately for polymer films. CE values for PProDOT-Me_2 have been measured relative to PEDOT and PProDOT, with values markedly higher from 183 mC/cm^2 for PEDOT to 375 mC/cm^2 for PProDOT-Me_2 at 95% of full contrast. We have investigated the use of BF_3 ethyl etherate as an alterative medium for the electrochemical synthesis of highly electroactive polymer films and have shown it to be applicable to preparing high quality polythiophene. Electrochromic devices (ECD's) with especially high color contrasts between bleached and colored states have been developed using cathodically coloring PProDOT-Me_2 and various anodically coloring polymers, especially the N-propane sulfonate derivative of poly(3,4-propylenedioxypyrrole) (PProDOP-NPrS). We have broadened the visible absorption in polymer ECD's while retaining the high contrast by having two cathodically coloring polymers with different λ_{max} values deposited as a bilayer on a single electrode using PEDOP (λ_{max} at 520 nm) and PProDOT-Me_2 (λ_{max} at 580 nm). By synthesizing polymers with especially low lying LUMO states using electron accepting moieties, in addition to the high lying HOMO states provided by electron rich heterocycles, we have develop electrochromic polymers having low band gaps and multi-colored states. This work has focused on silole and dicyanovinylene acceptors. The latter polymers could only be accessed using the BF_3 ethyl etherate polymerization medium described above. Functionalized 3,4-propylenedioxythiophene polymers have been developed as soluble conducting polymers for blending into elastomeric hosts and as solution processable high contrast electrochromic polymers. Finally, we have prepared multi-color electrochromic and red emitting polymers through the synthesis of soluble low band gap polymers containing conjugated donor and acceptor units.

3. Accomplishments

3.1 Electrochromic Polymers

3.1.a Defining Electrochromic Coloration Efficiencies. The use of colorimetry (color space mapping), spectroelectrochemistry, fluorescence spectroscopy, and coloration efficiency, among other methods have been utilized to help define the color of conducting polymers as well as other inorganic materials such as WO_3 and IrO_2. Coloration efficiency (CE) measurements, however,

have been somewhat of a "black art" in that different research groups have adopted different methods for analyzing this important property. Depending on the technique implemented and the type of device, very different values for CE can be obtained and have been reported. Therefore, we have developed a reproducible method which we hope will become a standard across the field by which CE can be measured accurately for polymer films. The method involves measuring the injected/ejected charge (doping level) as a function of unit area (Q_d) and the change in optical density ($\Delta OD(\lambda)$), that is the change in transmission at lambda max between the oxidized and reduced forms of the polymer film (Equation 1).

$$CE(\lambda) = \Delta OD(\lambda)/Q_d \qquad (1)$$

where $\Delta OD(\lambda) = \log[T_b(\lambda)/T_c(\lambda)]$.

The family of 3,4-alkylenedioxythiophenes (Figure 1) were chosen to probe this technique in which the substitution about the heterocycle was increased from ethylene (EDOT) to 2,2'-dimethylpropylene (ProDOT-Me_2).

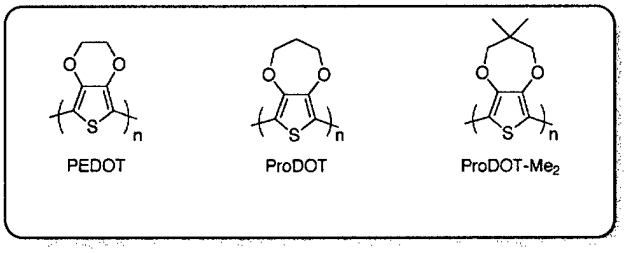

Figure 1. Poly(3,4-alkylenedioxythiophenes) used in CE experiments.

We have previously shown that by increasing the substitution in such a manner, the optical contrast can be significantly improved (72Δ%T for PProDOT-Me_2 vs. 51Δ%T for PEDOT), therefore an increase in the coloration efficiency should follow. The reasoning behind this is that a bulkier substitution pattern should result in a polymer film morphology that is more conducive to ion transport and higher doping levels. A more open morphology would allow the rapid movement of ions in and out of the polymer film, yielding a higher charge carrier content to effect a color change, thus increasing the coloration efficiency.

In the experiment, polymers were deposited electrochemically onto ITO-coated glass slides at constant potential to a specified thickness (1500 Å) to maximize the optical contrast. The polymers were then switched using square-wave voltammetry, while simultaneously monitoring the UV-vis absorbance at λ_{max} (Figure 2). Final CE values were obtained at 95% of the full contrast of the polymer since beyond it, the human eye cannot distinguish further color change, and to set a standard for future measurements.

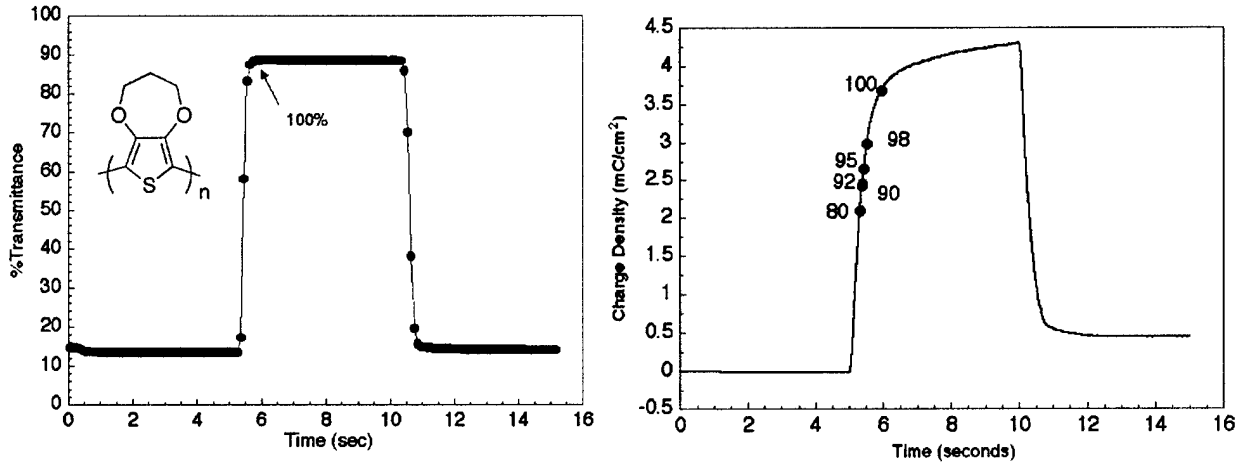

Figure 2. Tandem chronoabsorptometry (left)/chronocoulommetry experiment (right) showing one switch of a PProDOT film.

As can be seen in Figure 2, 100% of full contrast of the polymer is achieved quickly in the optical experiment once the current is applied. In this experiment it is important to determine the time required for full contrast (100% point on right) since the charge passed will continue to increase due to background current. By sampling at higher charge densities (times longer than required for the full optical switch) the resultant CE value is lowered even though the polymer has reached it maximum contrast at much lower charge levels.

The CE values for the three polymers studied were determined at varying percentages of full contrast (from 80% to 100%). Figure 3 (left) shows the expected enhanced CE displayed in PProDOT-Me_2 compared to PEDOT and PProDOT, with values markedly higher from 183 mC/cm^2 for PEDOT to 375 mC/cm^2 for PProDOT-Me_2 at 95% of full contrast.

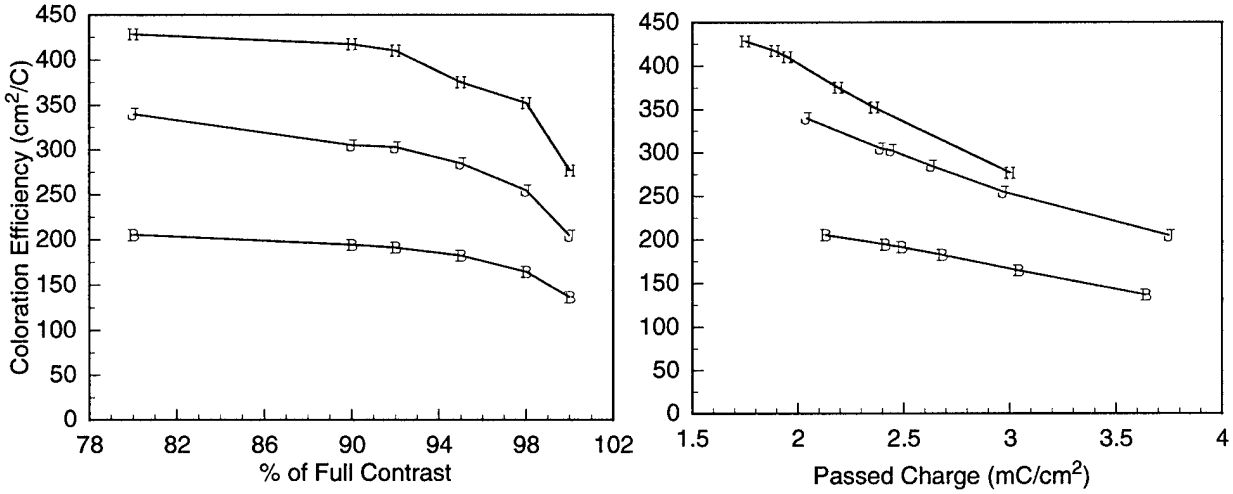

Figure 3. (Left) Plot of CE vs. the % of full contrast for three polymers. (Right) Plot depicting the decrease in CE as a function of increased charge passed at specific % of full contrast values (80% – 100%).

The right hand plot of Figure 3 demonstrates that by sampling at higher passed charge values, the CE of each polymer decreases. This exemplifies the fact that care must be taken when measuring this quantity to ensure that the maximum optical change is achieved with the minimum amount of charge passed to optimize the CE values.

In summary, the higher CE values for PProDOT-Me_2 may be attributed to the more open morphology of the polymer film. Even more highly substituted 3,4-alkylenedioxythiophenes may result in greater coloration efficiencies based upon the evidence presented here. This evidence is also encouraging since device applications require polymers that color and bleach rapidly over many switching cycles.

3.1.b Polymerizing "Difficult" Heterocycles. We have investigated the use of BF_3 ethyl etherate as an alterative medium for the electrochemical synthesis of highly electroactive polymer films. The use of this solvent in the synthesis of strong and highly conducting polythiophene (PTh) and poly(3-methylthiophene) (PMTh) has previously been demonstrated, however there is a lack of fundamental electrochemical and spectroelectrochemical data available to fully explain the role of the BF_3 complex in the polymer 'doping' process. The goal of this work was to extend the electrochemical synthesis utilizing BF_3 ethyl etherate to "difficult to polymerize"monomers that have high oxidation potentials.

Thiophene and 3-methyl thiophene were successfully polymerized on platinum, stainless steel and ITO coated glass substrates, from a solution containing monomer (0.01M) in BF_3 ethyl etherate. In both cases, homogenous films were grown at lower potentials than required for polymers grown in acetonitrile (ACN) or propylene carbonate (PC). There was a dramatic improvement with respect to the ease of film growth when using BF_3 ethyl etherate. Polymers were characterized by CV, DPV and spectroelectrochemistry in both BF_3 ethyl etherate and $LiClO_4$ (0.1 M)/ACN. Figure 4 shows the current response during the electrochemical deposition of polythiophene by CV, along with the scan rate dependence and spectroelectrochemistry of the resultant polymer.

The main figure clearly shows the efficient polymerization of thiophene with the evolution of polymer oxidation and reduction peaks. The scan rate dependence CVs illustrate the non-diffusion limited reversible nature of the oxidation and reduction responses of the polymer. Spectroelectrochemistry of polythiophene shows the formation of a polaron band upon oxidation of the polymer, which gives way to a bipolaron band at longer wavelengths as the polymer is more fully oxidized. These are far and above the "best" results obtained for PTh obtained directly from thiophene polymerization to date. Attempts to extend this methodology to 3,4-ethylenedioxythiophene (EDOT) were unsuccessful as EDOT is likely too electron rich to be stable in BF_3 ethyl etherate.

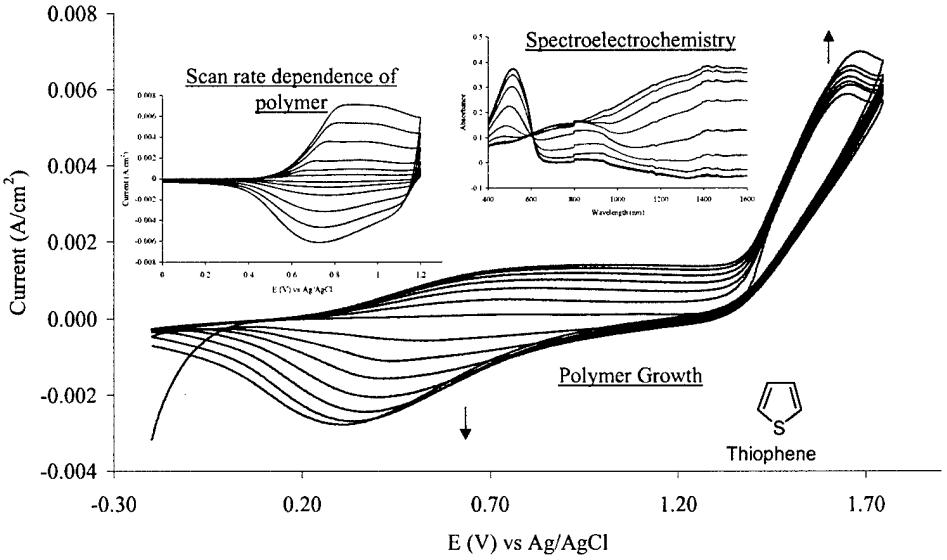

Figure 4. PTh electrosynthesized from a solution containing Th(0.01M)/ BF_3 ethyl etherate at 100mV/s. The scan rate dependence of the polymer was carried out in $LiClO_4$ (0.1M)/ACN vs Ag/Ag^+, scan rates are 10,20,50,100,200,300 mV/s. Spectroelectrochemistry was carried out in $LiClO_4$ (0.1M)/ACN vs silver wire.

3.2 Electrochromic Devices.

3.2.a High Contrast and Wide Band Electrochromic Devices

Our efforts in electrochromic devices (ECDs) have been directed towards attaining extremely high contrast by designing new low gap and especially high band gap polymers with suitable properties. The construction of a transmissive sandwich device shown schematically in Figure 5, is carried out with one polymer doped while the other one is neutral, making both either transmissive or absorptive, and the device bleached or colored. One focus has been the comparison of devices that have the same cathodically coloring polymer (PProDOT-Me_2) and have different anodically coloring polymers (including the N-propane sulfonate derivative of poly(3,4-propylenedioxythiophene) (PProDOP-NPrS)) developed in our group.

Figure 6 shows the transmittance spectra of the devices with poly(N-methyl-3,6-(BEDOT)carbazole)) (PBEDOT-NmeCz) (**A**) and PProDOP-NPrS (**B**) as the anodically coloring polymers and the insets are photographs with the devices in the two extreme states. The device **A** shows a maximum contrast of 56 % at 580 nm with the PBEDOT-NmeCz. The π–π^* transition of the neutral carbazole polymer is evident in the visible region and consequently causes the region between 400 and 500 nm less transparent. Using the PProDOP-NPrS in B opens up the transmissivity window through the entire visible spectrum, as well as considerably increasing the contrast between the bleached and the colored states to up to a 68% transmittance change.

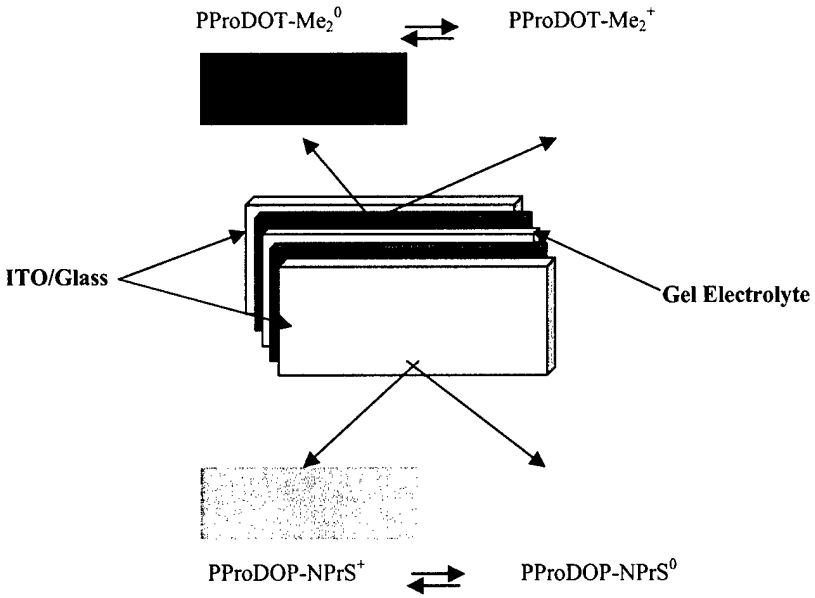

Figure 5. Schematic depicting the layering of electrochromic polymers for device fabrication.

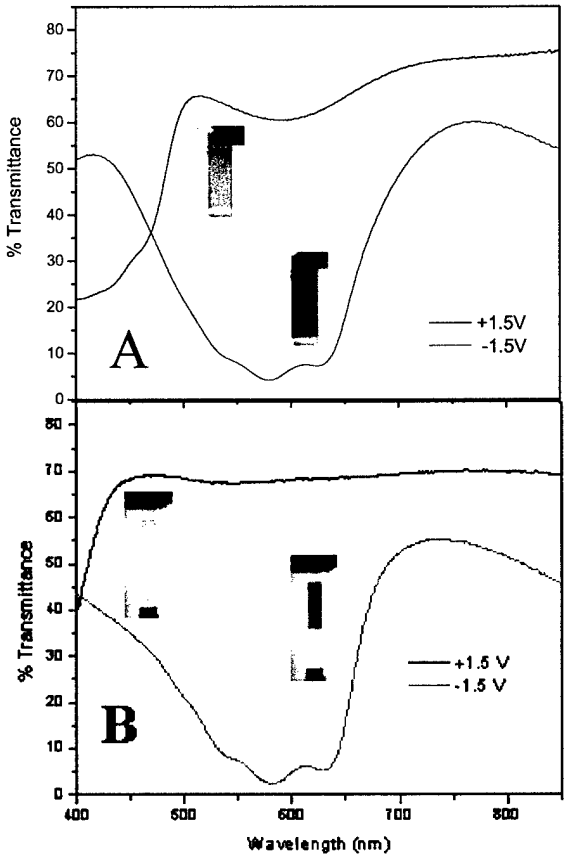

Figure 6: (**A**) Δ%T of PProDOT-Me_2/PBEDOT-NMeCz device. (**B**) Δ%T of PProDOT-Me_2/PProDOP-NPrS device.

Both devices switch as fast as the PProDOT-Me_2 alone (about 500 ms for 95% change in transmittance), as seen in Figure 7. For this experiment, the devices transmission was monitored at 580 nm and devices were cycled between the two color states and compared to a PProDOT-Me_2 film alone. The important concept seen in device **B** is that it has only a 6% contrast loss when compared to a PProDOT-Me_2 film alone (76% ΔT) upon adding the PProDOP-NPrS layer.

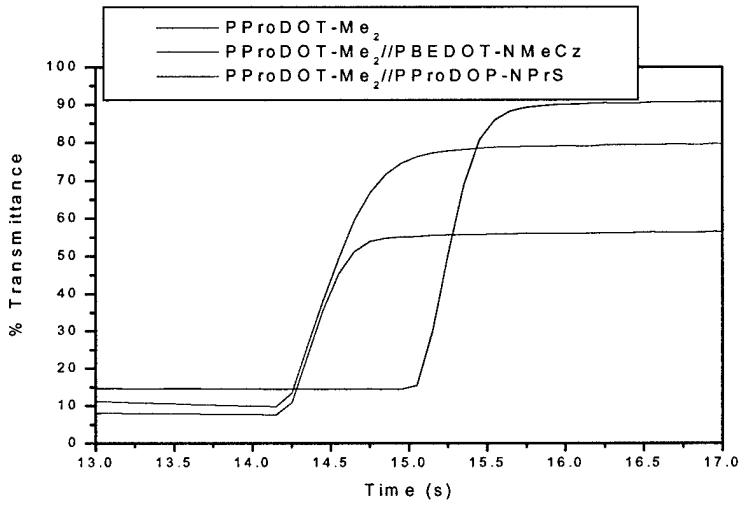

Figure 7. Switching times of PProDOT-Me_2 film, PProDOTMe_2//PProDOP-NPr and PProDOT-Me_2//PBEDOT-NMeCz

Figure 8 shows the colorimetric analysis for device **A**. We note that the device has a 62 % change in luminance (in essence the effective transmissivity sensed by a human eye) when switched between the bleached and colored state. The inset represents the x-y coordinates of the CIE color space, and for our device shows a change from a dark blue to almost clear blue-green color.

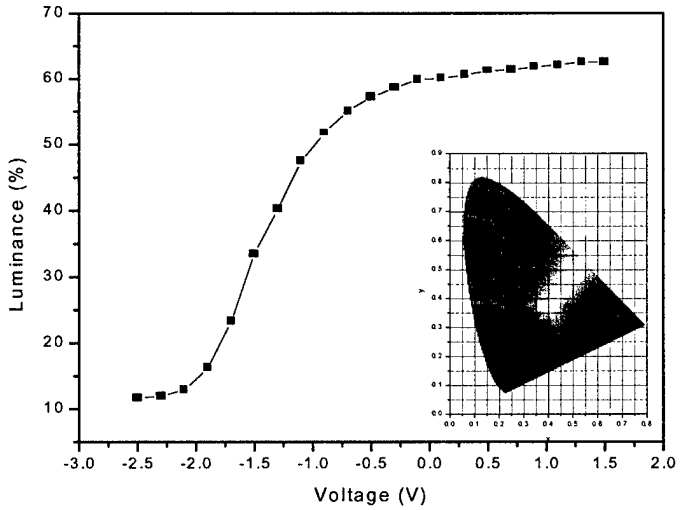

Figure 8. Colorimetric analysis of PProDOT-Me2//PProDOP-NPrS device.

The lifetime study shown in Figure 9 was carried out by continuously switching the device between the two extreme states and taking luminance measurements as a function of the number of redox cycles. The black trace (top) represents the decrease in the luminance of the bleached state of the device, while the red trace (top) is the lightening of the dark state during continuous switching. We noticed that the device loses some of its contrast (10%) before reaching 500 cycles. After this conditioning period, the degradation is extremely slow, the device showing 50% luminance change after 20,000 cycles (6 days of continuous switching).

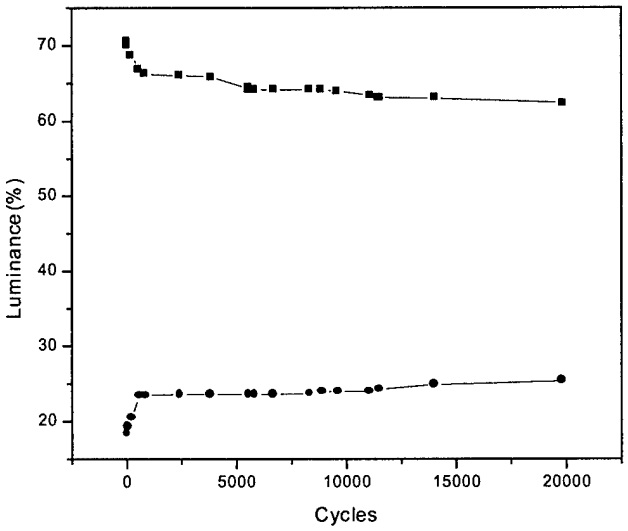

Figure 9. Lifetime of PProDOT-Me2//PProDOP-NPrS device.

In efforts to broaden the absorption peak while retaining the high contrast of our sandwich ECDs, we have explored the possibility of having two cathodically coloring polymers with different λ_{max} values deposited as a bilayer on a single electrode. We have used PEDOP (λ_{max} at 520 nm) and PProDOT-Me_2 (λ_{max} at 580 nm). The spectroelectrochemistry of the bilayer electrode is shown in Figure 10. At +1V, both polymers are in their oxidized form and the electrode appears transparent. As we started to decrease the potential to –1V, the peak corresponding to the π–π^* transition of the PProDOT-Me_2 layer could be seen at 580nm. In order to observe the π–π^* band transition in PEDOP film, a further decrease in the potential to -2V was necessary. When both polymers reached the neutral state a broadening as well as a large increase of the absorption peak could be seen.

The need for such a low reduction potential could be explained by the charge trapping mechanism outlined in Figure 11. When the polymers are oxidized, they are in their conducting form, bearing negative ions (ClO_4^-) within the films to counterbalance the positive charges on the backbone. At –1V, the PProDOT-Me_2 layer which is in direct contact with the solution becomes neutral expelling its dopant ions and causing it to be non-polar, making it more difficult for the PEDOP polymer to lose its dopant anions to solution. The difficulty in forcing anion transport through this medium is overcome at –2V. Further quartz crystal microbalance studies are necessary to validate this theory.

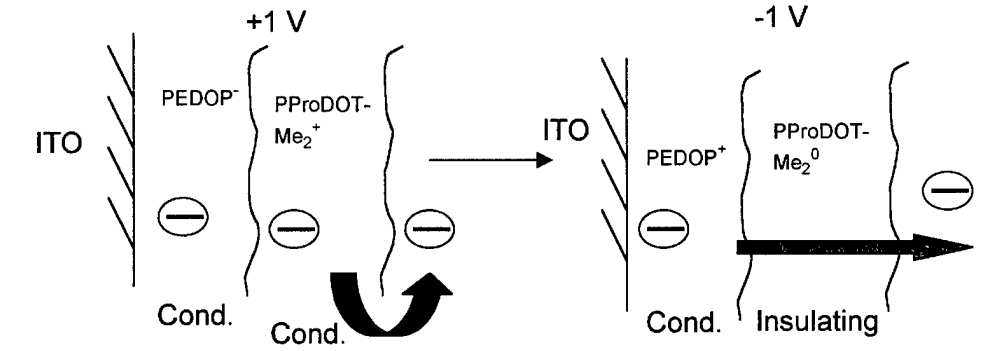

Figure 11. Bilayer concept.

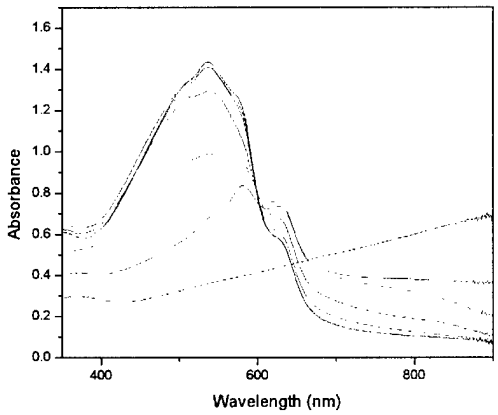

Figure 10. PEDOP/PProDOT-Me2 bilayer from +1V to –2V vs. Ag wire.

Figure 12 shows the absorption spectrum of a laminate device based on the above mentioned bilayer electrode and PBEDOT-NMeCz as the complementary high band gap polymer. This device shows a contrast of about 30% transmittance change when the device is switched from +2V to –4V. Further studies with the newly discovered PProDOP-NPrS as the high band gap polymer are underway in our labs.

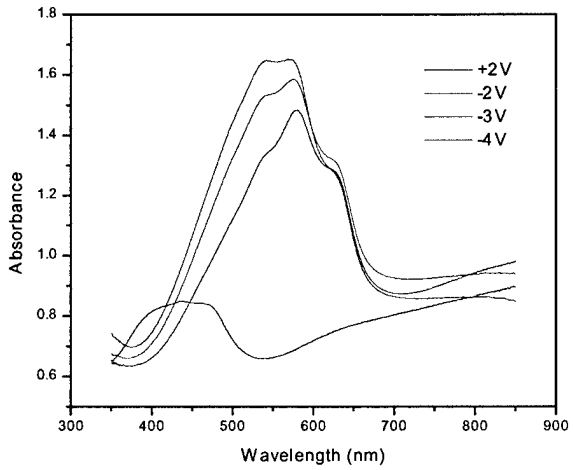

Figure 12: PEDOP/PProDOT-Me_2//PBEDOT-NMeCz device spectroelectrochemistry.

3.3 Low Band Gap and Multi-Color Electrochromic Polymers

By synthesizing polymers with especially low lying LUMO states using electron accepting moieties, in addition to the high lying HOMO states provided by electron rich heterocycles, we develop electrochromic polymers having multi-colored states. For example poly(bis(EDOT)pyridine) is magenta-red in its neutral form, deep blue-purple in its p-doped state, and sky blue in its n-doped state.

3.3.a Silole Containing Electrochromic Polymers. Due to its unique electronic structure, the silicon atom in silole provides a low-lying LUMO state. We have synthesized a new electroactive silole-containing polymer with the goal of attaining a low band gap, and possibly introducing multi-color electrochromism as shown in Figure 13. To accomplish this, a new silole containing monomer, 1,1-dihexyl-3,4-diphenyl-2,5-bis{2-(3,4-ethylenedioxy)thienyl}silole, (BEDOT-Silole), was synthesized by a Pd-catalyzed cross coupling reaction of the 1,1-dihexyl-3,4-diphenyl-2,5-dibromosilole and 2-stannyl-EDOT in THF.

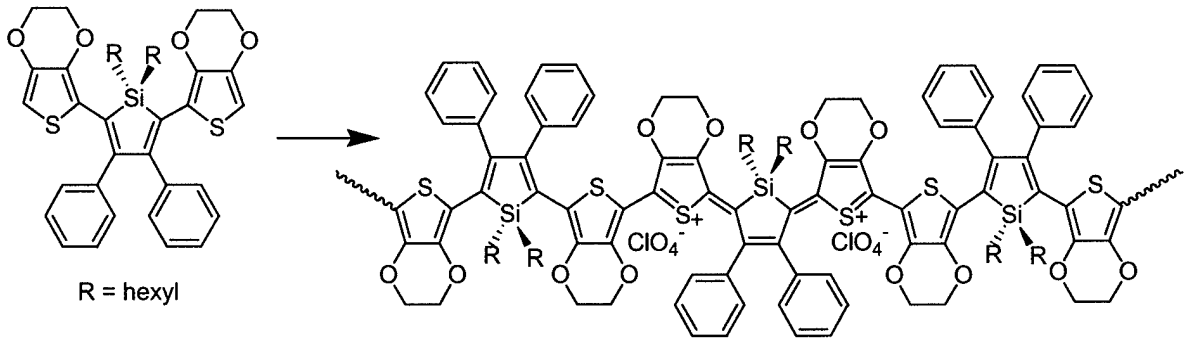

Figure 13. Oxidative polymerization of BEDOT-Silole

Poly(BEDOT-Silole) was synthesized utilizing repeated potential scan electrochemical polymerization at a scan rate of 100 mV/s in 0.01 M monomer and 0.1 M $LiClO_4$ in a mixed solvent system of acetonitrile (ACN) and water (90/10, v/v) using a bare glassy carbon working electode and a Fc/Fc^+ reference electrode. A peak for monomer oxidation ($E_{p,m}$) is observed at 0.29 V vs. Fc/Fc^+ and a rapid and regular growth of the polymer on the electrode was observed. The oxidative peak of the polymer is observed at -0.01 V and two reduction peaks are observed at -0.19 V and -0.35 V with a half wave potential ($E_{1/2,p}$) at -0.13 V for the main redox process.

Poly(BEDOT-silole) films were electrochemically deposited on ITO-coated glass for spectroelectrochemical studies as shown in Figure 14. The spectra were initially obtained in the fully reduced state in order to determine the band gap of the polymer. The low-lying LUMO levels of the siloles, combined with the electron-rich character of the 3,4-ethylene dioxythiophene units confer upon this new polymer a low band gap of 1.3~1.4 eV. The electrochromic properties of this polymer were also studied by in situ colorimetry. Poly(BEDOT-Silole) changes from blue in its reduced form to transmissive yellow-green upon oxidation.

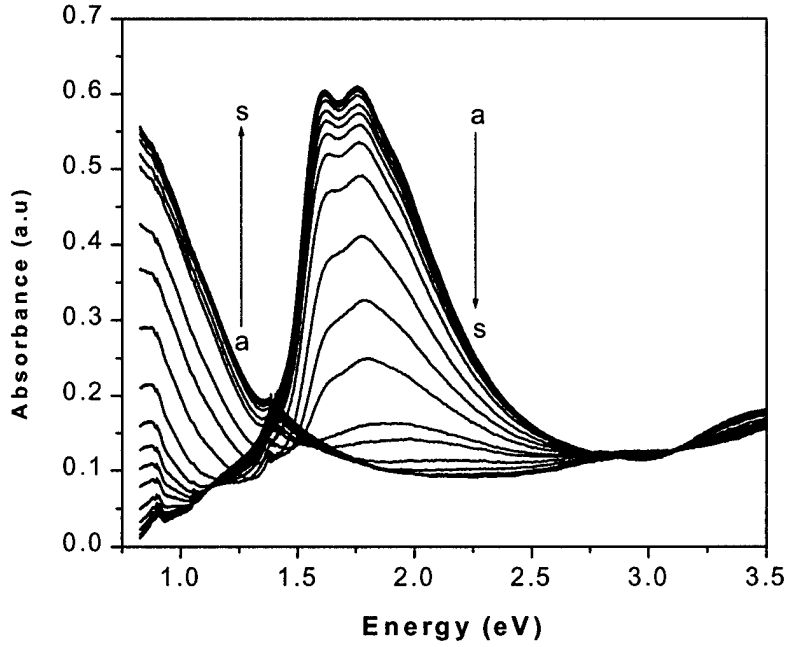

Figure 14. Spectroelectrochemical analysis of poly(BEDOT-Silole) in 0.1 M $LiClO_4$ / PC at applied potentials of (a) → (s): -0.43 V→ 0.17 V vs. Fc/Fc^+ in 20 mV potentials steps.

3.3.b Dicyanovinylenes With Increased Acceptor Character

The polymerization of 1,2-bis(2-thienyl)-1,2-dicyanovinylene (BTh-$(CN)_2$V) was attempted in monomer/electrolyte solutions containing TBAP(0.1M)/ACN and $LiClO_4$ (0.1 M)/PC using potentiostatic, galvanostatic and potentiodynamic growth methods, *all of which were unsuccessful*. However, monomer solutions containing 0.01M BTh-$(CN)_2$V in BF_3 ethyl etherate *were found to successfully yield polymer films* upon electrooxidation. Figure 15 shows the repeated scanning deposition of BTh-$(CN)_2$V, and is indicative of an efficient electropolymerization. CVs and DPVs of the polymer itself (also shown in Figure 15) show the presence of a reversible oxidation response, as well as a reversible redox response at more cathodic potentials. If this response is attributed to n-doping of the polymer film, the band gap may be as low as 0.45 eV, and further work is being directed to this polymer. Extending the cathodic limits of the CV of P BTh-$(CN)_2$V reveals the presence of a second reversible reduction response (Figure 16). The current response of the scan rate dependence also appears to be non-diffusion limited.

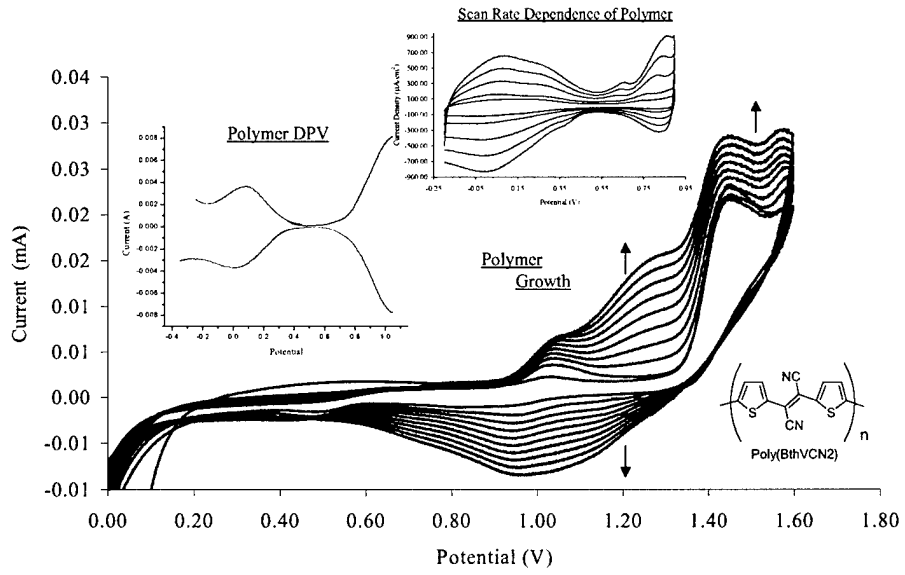

Figure 15. Electropolymerization and redox switching of the resultant polymer for 0.01M BTh-$(CN)_2V$ in BF_3 ethyl etherate at a scan rate of 100 mV/s vs Ag/AgCl. The scan rate dependence of the polymer was run in TBAP (0.1M)/ACN vs Ag/Ag^+, scan rates were 20, 50, 100, 200, 300 mV/s. The DPV was also run in TBAP (0.1M)/ACN vs Ag/Ag^+.

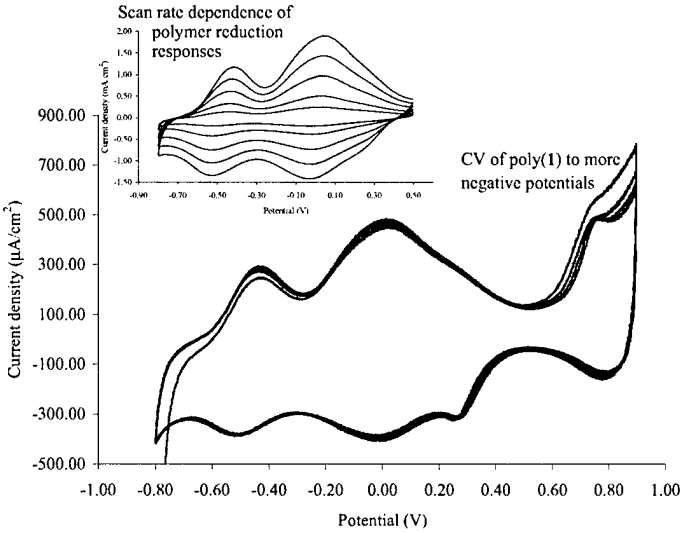

Figure 16. Cathodic electrochemistry of P BTh-$(CN)_2V$. The electrolyte solution was TBAP (0.1M)/ACN the scan rate was 50 mV/s (vs Ag/Ag^+). Scan rate dependence covered scan rates of 20,50,100, 200, 300 mV/s.

Spectroelectrochemistry of this polymer found no change in the UV-visible/near IR spectra of the polymer over the wavelength range 300-2700 nm in either the reduced or oxidized form, despite the polymer still being electroactive by CV. This may suggest the band gap is lower than the limits of this experiment.

3.4 Soluble and Processable Electroactive Polymers

3.4.a Soluble PProDOTs for Blending

We have selected the functionalized 3,4-propylenedioxythiophene polymer family for development into soluble conducting polymers. As the propylene bridge can be disubstituted, the monomers are symmetric and this yields regiosymmetric conjugated polymers. We expect these regular polymers to yield high conductivity upon doping due to order induced upon processing. An important finding in these PProDOTs was that as the size of the substituents, and as the degree of substitution, increased, the electrochromic contrast ratio increased and the switching time decreased. The substituents were hypothesized to produce a more open morphology in the polymer, which increased the ion flux and allowed for a greater degree of doping occurring in an electrochromic device.

Polymers of this type are nicely prepared via the Grignard Metathesis (GriM) polymerization elucidated by Rick McCullough's group. We found that the dibutyl derivative of PProDOT-Bu_2 had a somewhat limited solubility, so work was directed to preparing PProDOT's with long chain substituents (Figure 17). ProDOT($CH_2OC_{18}H_{37}$)$_2$ was brominated at the 2 and 5 position on the thiophene ring using NBS in chloroform. This crystalline solid had a low melting point and was purified by column chromatography. Since Grignard metathesis is extremely sensitive to the stoichiometry of the reagents, the monomer was purified through two chromatography columns to ensure purity.

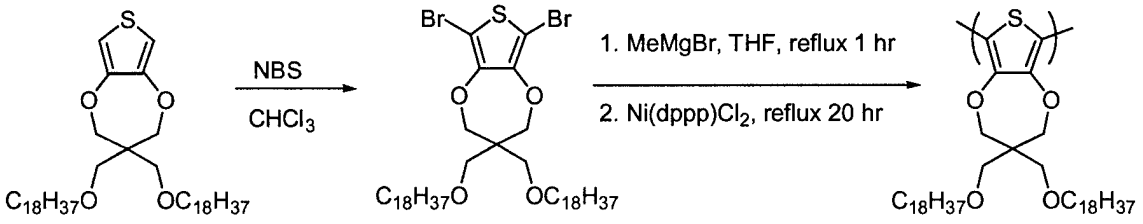

Figure 17. ProDOT($CH_2OC_{18}H_{37}$)$_2$ bromination and GriM polymerization.

After polymerization and purification, the polymer was dissolved in methylene chloride and purple freestanding films could be cast. The cyclic voltamogram of PProDOT(CH_2OC_{18})$_2$ was performed on films on a Pt button. The CV was taken in a 0.1 M TBAP acetonitrile solution with a Pt flag working electrode and an Ag wire as a reference. The CV shows a reversible redox system with an $E_{1/2}$ of 0.37 V vs Ag/Ag^+.

Spectroelectrochemistry was performed by first casting a film of the polymer onto an ITO slide. The same solvent system and electrodes used while taking the CV were employed. The first spectrum, with the voltage set at -1.0 V vs Ag wire, gave the neutral π to π^* transition with a λ_{max} at 589 nm as shown in Figure 18. Spectra were taken at 0.3, 0.4, and 0.5 V showed very little change. The spectrum taken at 0.6 V shows a drastic change, with a large drop in absorbance in the visible region. An absorption evolves around 1000 nm typical of a polaronic charge carrier. As the voltage increased to 0.7, 0.8 and 0.9 V, the absorbance in the visible region dropped slightly while the absorbance in the IR region increased dramatically. These IR peaks are most likely caused by bipolaron transitions. The high degree of contrast observed in the visible region is encouraging for solution cast films in electrochromic devices and will be pursued further.

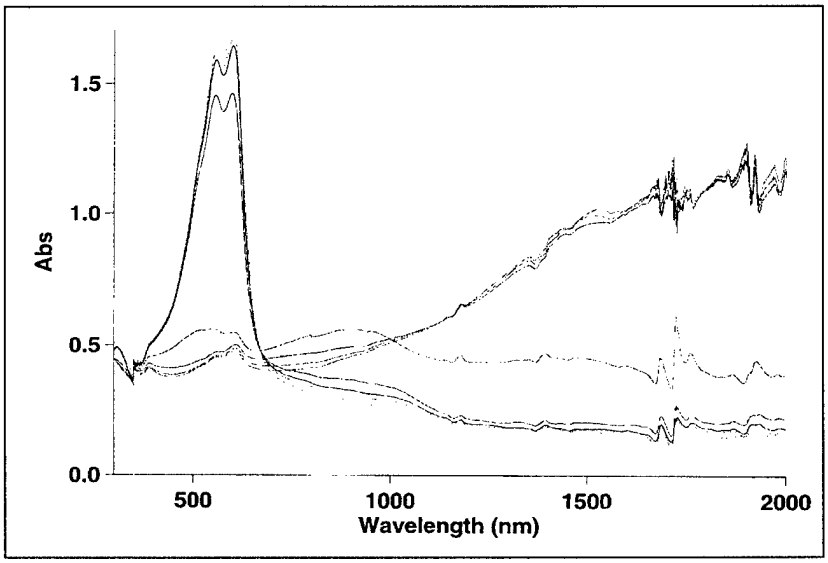

Figure 18. Spectroelectrochemistry of a cast film of PProDOT($CH_2OC_{18}H_{37}$)$_2$ on an ITO plate in a 0.1 M TBAP solution in acetonitrile. The spectra were taken at -1.0 V, 0.3 V, 0.4 V, 0.5V, 0.6 V, 0.7 V, 0.8 V, and 0.9 V vs Ag wire.

The fact that these alkyl PProDOTs oxidatively dope as well as they do has now led us to begin scaling up the synthesis to produce sufficient material for blending with an elastomeric host. Additional funding has been provided from AFOSR via AFRL to accomplish this. Conductivity:composition profiles will be developed in order to examine the possibility of creating a conducting elastomer.

3.4.b Soluble Donor Acceptor Polymers

In order to prepare multi-color electrochromic and red emitting polymers for LEDs, we have pursued the synthesis of soluble low band gap polymers containing conjugated donor and acceptor units. The monomers used in this work are shown with the synthetic schemes used to attain them in Figures 19 and 20.

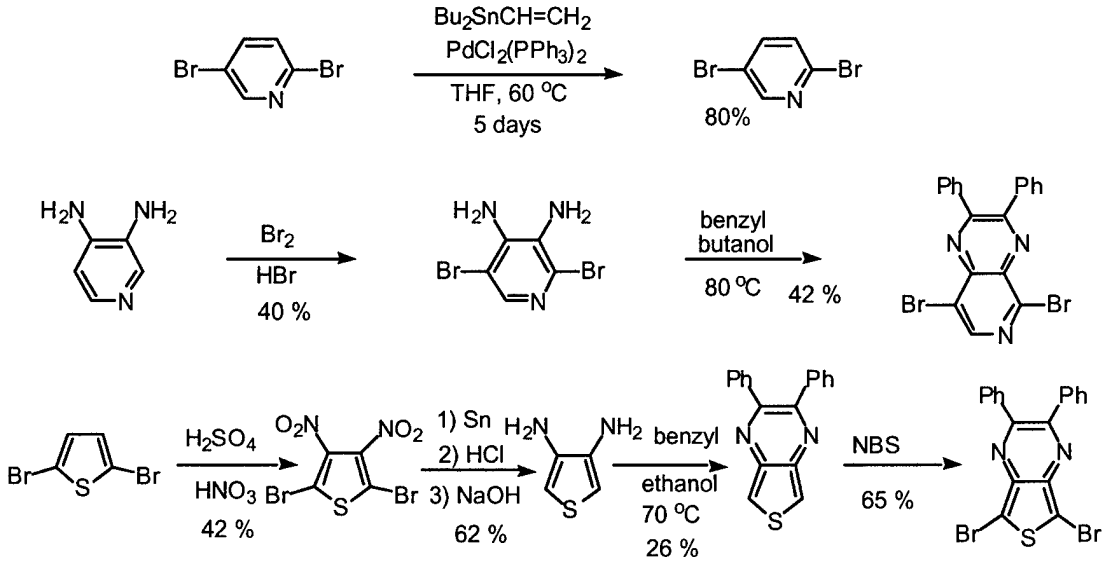

Figure 19. Synthesis of acceptor monomers

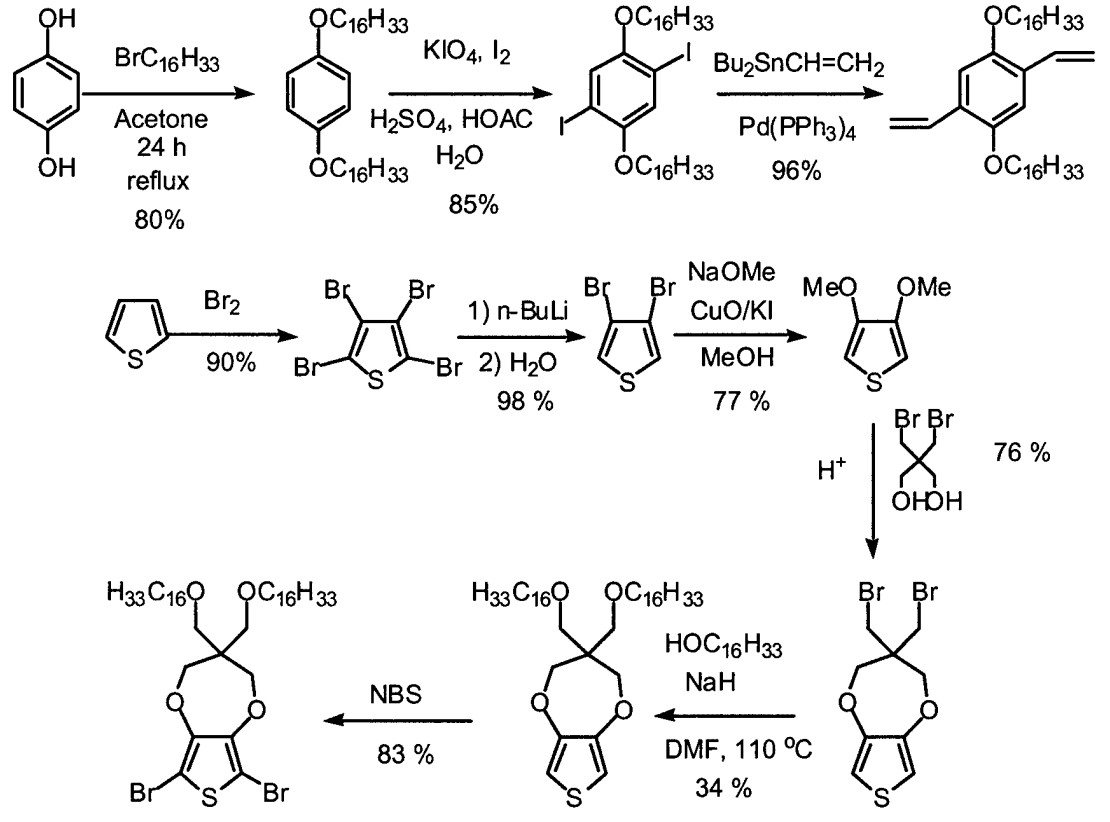

Figure 20. Synthesis of donor monomers

Polymers have been prepared as shown in Figures 21 and 22. In optimizing polymerization conditions, we followed the purity of the monomers by using the ^{13}C NMR satellite technique. In this technique any impurity is calculated based on the ^{13}C-satellite peak of the monomer. The advantage of using this technique is that the error in calculating the quantity of impurity is reduced by comparing areas of the same relative signal to noise ratio.

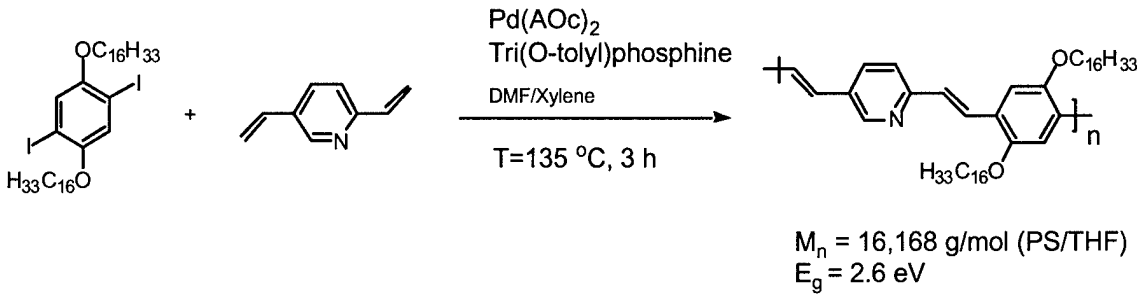

Figure 21. Synthesis of Poly(pyr-V-B($OC_{16}H_{33}$)-V)

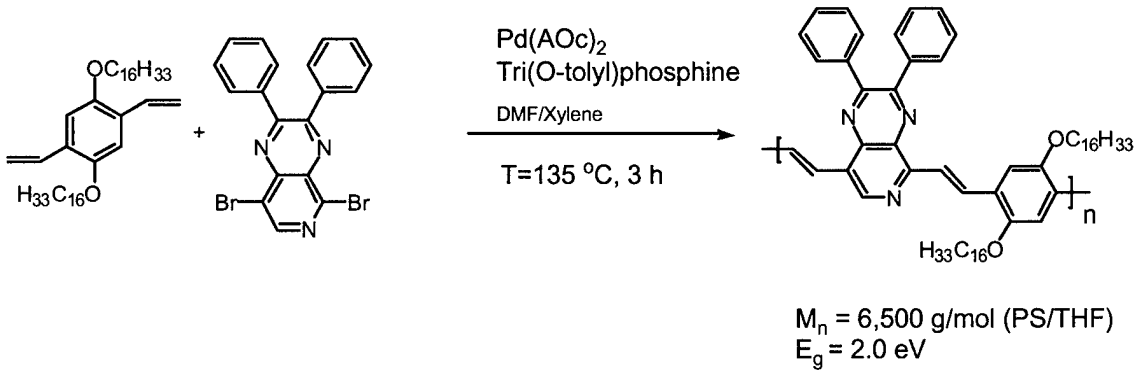

Figure 22. Synthesis of Poly(pyrpyr-V-B($OC_{16}H_{33}$)-V)

Figure 23 shows the absorption and luminescence spectra of both polymers where their syntheses were detailed in Figures 21 and 22. It is evident that by using the stronger pyridopyrazine acceptor, in place of pyridine, there is a distinct red shift in the luminescence spectrum. Poly(pyr-V-B($OC_{16}H_{33}$)-V) shows a green luminescence with two emission maximaat 540 and 590 nm respectively. On the other hand, poly(pyrpyr-V-B($OC_{16}H_{33}$)-V) shows a red luminescence with an emission maximum at 650 nm.

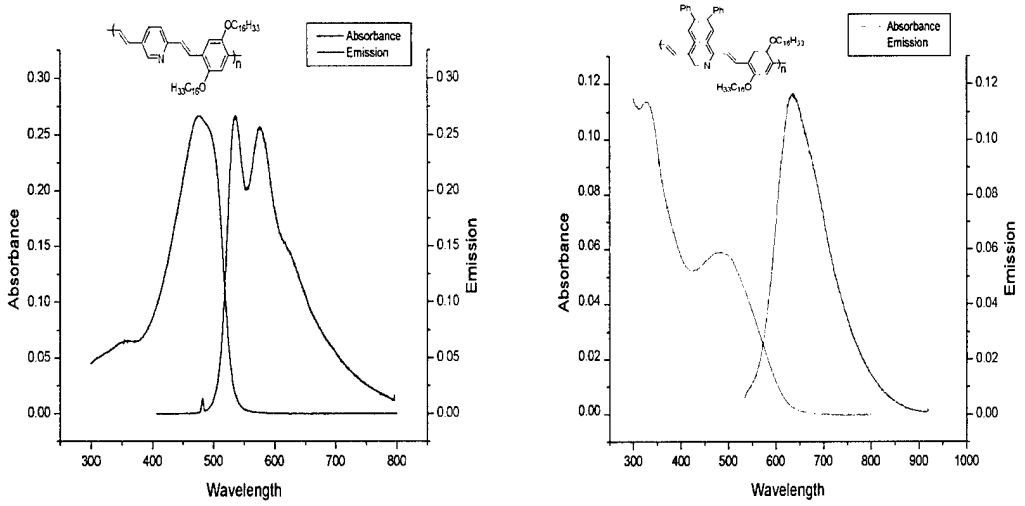

Figure 23. Absorption and luminescence spectra of both Poly(pyr-V-B($OC_{16}H_{33}$)-V) and Poly(pyrpyr-V-B($OC_{16}H_{33}$)-V)

Personnel Supported:

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Carl Gaupp
Charles DuBois
Dean Welsh

Peer Reviewed Publications

1. Hopkins, A. R., Reynolds, J. R.
Macromolecules, **33**, 5221-5226 (2000).
"Crystallization Driven Formation of Conducting Polymer Networks in Polymer Blends"
(Funding via AFOSR/BMDO sub-contract from Gemfire Corp.)

2. Sonmez, G., Schottland, P., Zong, K., Reynolds, J. R.
J. Mater. Chem., **11**, 289-294 (2001).
"Highly Transmissive and Conductive Poly(3,4-alkylenedioxypyrrole) (PXDOP) Films Prepared by Air or Transition Metal Catalyzed Chemical Oxidation"

3. Irvin, J. A., Schwendeman, I., Lee, Y., Abboud, K. A., Reynolds, J. R.
J. Polym. Sci., Polym. Chem., **39**, 2164-2178 (2001).
"Low Oxidation Potential Conducting Polymers Derived from 3,4-Ethylenedioxythiophene and Dialkyoxybenzenes"

4. Lee, Y., Sadki, S., Tsuie, B., Reynolds, J. R.
Chem. Mater., **13**, 2234-2236 (2001).
"A New Narrow Band Gap Electroactive Polymer: Poly[2,5-bis-(2-{3,4-ethylenedioxy)thienyl}silole]"

5. Reynolds, J. R., Epstein, A. J.
Adv. Mater., **12**, 1565-1570 (2000).
"ICSM 2000: Over Twenty-Five Years of Synthetic Metals"

6. Giurgiu, I, Reynolds, J. R., Lee, W.-P., Brenneman, K. R., Saprigin, A. V., Epstein, A. J., Hwang, J., Tanner, D. B.
Syn. Met., **119**, 405-406 (2001).
"Dioxypyrrole and Dioxythiophene Based Conducting Polymers: Properties and Applications"

7. Thompson, B. C., Schottland, P., Sonmez, G., Reynolds, J. R.
Syn. Met., **119**, 333-334 (2001).
"*In Situ* Colorimetric Analysis of Electrochromic Polymer Films and Devices"

8. DuBois, C. J., Jr., Larmat, F., Irvin, D. J., Reynolds, J. R.
Syn. Met., **119**, 321-322 (2001)
"Multi-colored Electrochromic Polymers Based on BEDOT-Pyridines"

AFOSR Funded Publications In Press and Submitted

1. Zong, K., Reynolds, J. R.
J. Org. Chem., accepted for publication
"3,4-Alkylenedioxypyrroles: Functionalized Derivatives as Monomers for New Electron-Rich Conducting and Electroactive Polymers"

TRANSITIONS

1. a) Reynolds/Florida, b) High contrast, broad band electrochromic devices, c) Dr. Tim Bunning (AFRL/MLPJ, timothy.bunning@wpafb.af.mil), d) Laminate film electrochromic device results have been supplied to AFRL with interests in broadband absorption.

2. a) Reynolds/Florida, b) Water soluble PEDOTs for electrostatic adsorption processing, c) Dr. Jeff Baur and Michael Durstock, AFRL/MLBP (Michael.durstock@afrl.af.mil, 937-255-9208), d) Polymers for photovoltaic devices. Successful development of polymer-based PV devices require donor and acceptor polymers with controlled band states. Electron rich water soluble PEDOTs have been supplied for ESA processing and use as electron donor components in photovoltaic devices.

3. a) Reynolds/Florida, b) 3,4-Alkylenedioxythiophene polymers, c) Bert Groenendaal, Agfa Gaevert, Belgium (32 3 444 32 24), d) Agfa is developing, in collaboration with the Reynolds group, new routes to 3,4-ethylenedioxythiophene and related polymers.

4. a) Reynolds/Florida, b) Drs. David Rauh and Fei Wang, EIC Laboratories (781-769-9450), d) "Multi-color Electrochromic Camouflage", Contract #DACA41-01-C-011. A variety of the electrochromic systems developed by the Reynolds group are being applied to electrochromic devices at EIC.

5. a) Reynolds/Florida, b) Redox switchable conducting polymers for microwave devices, c) Dr. John Stenger-Smith, Naval Air Warfare Center, China Lake, CA (760-939-1661), d) Electrochromic polymers developed in AF funded program demonstrate excellent microwave switching properties for electromagnetic shutters with application to radar and antenna type devices.

6. a) Reynolds/Florida, b) Redox switchable conducting polymers for modulating infrared reflectivity from metals, c) Dr. Henry Everitt and Dr. Jack Rowe at ARO (919-549-4369), Program and ARO/IR MURI, d) Electrochromic polymers developed in AF funded program demonstrate excellent contrast and switching properties in reflective devices for controlling IR reflectivity off of a metallic surface. Application to controlled emissivity surfaces and camouflage.

7. a) Reynolds/Florida, b) Reflective electrochromic devices, c) Dr. Heyward Robinson, SRI International (650-859-3867), d) EC devices prepared by the Reynolds group have been supplied to SRI for analysis of mid- to far-IR modulation of reflectivity off a metal surface.

8. a) Reynolds/Florida, b) Printable conducting polymers, c) Dr. Danielle Boils, Xerox Company (905-823-7145, ext. 309), d) Xerox is investigating soluble PProDOTs as potentially ink jet printable conducting polymers.

Awards and Honors received by the PI (life-time received):

University of Florida, Research Foundation Fellowship 1999